

(12) UK Patent Application (19) GB (11) 2 148 871 A

(43) Application published 5 Jun 1985

(21) Application No 8426002	(51) INT CL ⁴ C04B 14/42 14/04 14/22		
(22) Date of filing 15 Oct 1984	(52) Domestic classification C1H 120 620 710 717 726 742 782 D1R 101 303 318 514 515 547 551 553 603 DC U1S 1699 1700 C1H D1R		
(30) Priority data	(56) Documents cited None		
(31) 8328982 8409160	(32) 31 Oct 1983 9 Apr 1984	(33) GB	(58) Field of search C1H C3N D1R
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(54) Sheet material of fibre-reinforced cement

(57) Sheet material, which may be flat or of profiled (e.g. corrugated) cross-section, suitable for use as building panels, e.g. roofing slates, is formed of a fibre-reinforced cement composition comprising, in weight percentages:-

Ordinary Portland cement	50 to 71%
Pulverised fuel ash	14 to 40%
Volatilised silica (containing at least 86% SiO ₂)	5 to 12%
Filamentised chopped glass fibre strands	2 to 7%

these components constituting at least 90% by weight of the composition, the material having a minimum average modulus of rupture of 16 N.mm⁻² and a minimum density of 1.3 g.cm⁻³. The balance of the composition may include up to 4% by weight cellulose pulp and up to 5% of a plasticiser such as ball clay, bentonite or talc, together with small quantities of known dispersing agents and flocculating agents.

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SPECIFICATION

Sheet material of fibre-reinforced cement

5 This invention relates to sheet material of fibre-reinforced cement, which may be flat or of profiled cross-section, e.g. corrugated. Such material is suitable for use as building panels, e.g. for roofing. The flat material is particularly suitable for use as roofing slates.

Sheet materials of cement reinforced with asbestos fibres have been known for many years and provide a lightweight roofing material which is both weather-resistant and fibre-resistant. There is now a need to 10 replace asbestos as a component of such materials, but the product obtained as a result of such replacement must be substantially equivalent to the existing asbestos-cement materials in all their desirable properties. The materials must also be capable of being made on existing asbestos-cement equipment so as to avoid the capital cost of replacing or drastically altering such equipment.

15 The use of glass fibre as a replacement for asbestos fibre in such equipment has been the subject of considerable research over the past 10 to 15 years. The problems originally encountered, which are discussed for example in our U.K. Patent Specification No. 1,543,951, have been overcome to the extent that it is now possible to formulate glass fibre-containing cement slurries which can be run on asbestos-cement machines, e.g. by the measures described in Specification No. 1,543,951. This ability is not necessarily accompanied by the production of a product with adequate properties for a particular purpose.

20 Sheets or panels for use in building generally require to have a mean modulus or rupture (bending strength) of at least 16 N.mm^{-2} and a density of at least 1.3 g.cm^{-3} . For roofing slates, the requirements are more stringent. Presently available asbestos cement roofing slates, otherwise known as compressed asbestos cement slates, have a smooth surface which generally carries an acrylic coating of the desired colour, and are required by current U.K. standard specifications to have an average minimum mean modulus 25 of rupture (MOR) of 22.5 N.mm^{-2} . A minimum density of 1.8 g.cm^{-3} is advisable to avoid porosity which could result in frost damage in roofing slates.

Simple replacement of the asbestos content of asbestos-cement sheet materials by glass fibre in chopped strand form does not produce materials of equivalent appearance, because the chopped strands tend to be visible in or to project from the surface, resulting in a surface finish which is either unacceptable when the 30 usual amount of coating has been applied or requires so much decorating material to produce an acceptable coating as to cause an unacceptable increase in cost. Furthermore such simple replacement of the asbestos by chopped strand glass fibre does not enable one to achieve equivalent strengths with economic amounts of glass fibre, due to uneven distribution of the glass fibre in the cement and attack on the glass fibre by the alkalis in the cement. In our U.K. Patent Specification No. 1,543,951 we have described a method of 35 manufacturing an asbestos-free fibre-reinforced cement composite material from an aqueous cement slurry incorporating both chopped strands of glass fibre and single filaments of inorganic non-crystalline material, which latter may be produced from continuous filament chopped glass fibre strands which separate or filamentise on contact with the cement slurry. If glass fibre in such single filament form produced from filamentised chopped strands is used as the sole fibrous reinforcement, a smooth surface finish can be 40 obtained. The strength problems are aggravated, however, because the single filaments are open to attack by the alkalis in the cement and there is also difficulty in achieving an adequate bond between the fibre and the matrix.

To improve the strength of glass fibre reinforced cement products, various proposals have been made for the incorporation of reactive silica in different forms. For example, U.K. Patent Specification No. 1,402,555 45 (N.R.D.C.) relates to a glass fibre reinforced pozzolanic cement product comprising a cement matrix containing at least 10% by weight of a pozzolana (which is a silicate glassy material capable of reacting with calcium hydroxide and thereby setting into a hard strong material) and fibres of an alkali-resistant silica/zirconia glass containing at least 6 mol. % ZrO_2 . The specification states that a very desirable increase in the strength of the composites may be obtained by controlled heat treatment which accelerates the 50 attainment of stable properties and ultimate strength and which may take the form of at least two days under water at a temperature of e.g. 60°C to 80°C . One of the preferred pozzolanas described is pulverised fuel ash (PFA) used in amounts from 15% to 40% by weight. U.K. Patent Specification No. 1,421,556 (TAC Construction Materials Limited) describes the production of cement board products reinforced with a mixture of long and short staple alkali-resistant vitreous fibres, e.g. chopped glass fibre strands and milled 55 mineral fibres, with cellulose fibre and sufficient silica, e.g. in the form of diatomite, to react with the free lime liberated during the hydration of the cement. The board products are autoclaved to assist the reaction. European Patent Application No. 68,742 (Cape Boards & Panels Limited) relates to shaped articles such as boards and sheets for cladding and roofing, and describes a manufacturing process using an aqueous slurry 60 comprises, on a dry weight basis, 50% to 90% cement, 5% to 40% highly reactive pozzolanic silica and 5% to 15% cellulose fibres. Reaction occurs between the cement and the silica by air curing. The specification states that mixtures of highly reactive pozzolanic silicas, e.g. volatilised silica and diatomite, may be used and that glass fibres may be incorporated in addition to the cellulose fibres. U.K. Patent Specification No. 2,048,300B (Rockwool International A/S) describes a method of preparing a fibre reinforced cementitious plate from an aqueous slurry of cement and fibres selected from the group consisting of synthetic mineral 65 fibres, natural organic fibres and mixtures thereof, wherein a fine material (specifically a filter dust produced

as a by-product in the manufacture of silicon or silicon alloys by an electrothermal process and consisting essentially of volatilised silica) having an average particles size lower than that of the cement particles is incorporated in the slurry to reduce the loss of fine cement particles and to neutralise alkaline products in the mixture, thus inhibiting alkaline degradation of the mineral fibres. It is said that the amount of fine particles

5 5 should preferably not exceed 15% by weight based on the weight of the cement because high concentrations of fine particles reduce the rate at which excess water is removed from the slurry. Finally in our own U.K. Patent Specification No. 1,565,823 we disclose the use of reactive silica in the form of pulverised fuel ash (PFA) or a fine silica flour such as diatomite or ELKEM silica which is a volatilised silica, which were found to have a synergistic effect with the particular size compositions described in that specification for application to

10 10 alkali-resistant glass fibres for reinforcement of cement. Proportions of 10% to 40% of the reactive silica were shown to produce a further improvement in durability of the sized glass fibre strands incorporated in the cement. We believe that the reactive silica assists in bonding the glass fibre into the cement matrix as well as reacting with alkalis in the matrix.

Our own recent investigations indicate that the various forms of reactive silica have different effects on the

15 15 early strength and on the long term strength of the composite materials. This is particularly the case where glass fibre in single filament form is used for reinforcement. Our investigations have shown that if one uses filamentised dispersible glass fibre strands as the sole fibrous reinforcing material, it is essential to use a mixture of two different reactive silicas, namely pulverised fuel ash and volatilised silica, within specific ranges, in order to be able to produce flat sheet material suitable for use as building panels on existing

20 20 asbestos-cement machinery, with both a good start strength and good long term durability, which can even be accompanied by an increase of strength beyond the initial strength. Use of the volatilised silica without the pulverised fuel ash gives a good start strength but on subjection to simulated ageing tests the material shows a marked falling off in strength. Pulverised fuel ash on its own without the volatilised silica gives a poor start strength and a poor overall matrix strength.

25 25 According to the invention, therefore, a sheet material is provided, formed of a fibre-reinforced cement composition comprising, in percentages by weight of solids:-

30	Ordinary Portland cement	50 to 71%	
	Pulverised fuel ash	14 to 40%	
	Volatilised silica (containing at least 86% by weight SiO ₂)	5 to 12%	30
	Filamentised chopped glass fibre strands	2 to 7%	

in which these components constitute at least 90% by weight of the solid constituents of the composition

35 35 and in which, when the cement composition comprises less than 8% by weight of volatilised silica, the volatilised silica is of a grade containing more than 86% by weight of SiO₂, and when the cement composition comprises only 5% by weight volatilised silica, the volatilised silica is of a grade containing at least 94% by weight SiO₂, the sheet material having a minimum average modulus of rupture of 16 N.mm⁻² and a minimum density of 1.3 g.cm⁻³.

40 40 The combination of pulverised fuel ash and volatilised silica in the proportions set out above results in a product with a satisfactory initial strength and long term durability, accompanied by an increase of strength beyond the initial strength after curing. The use of filamentised glass fibre produces a smooth surface, as required where a coating is to be applied, by avoiding the occurrence of projecting strand ends as would occur if integral chopped strands were used.

45 45 The term "volatilised silica" is used herein to describe the material (otherwise known as microsilica or silica fume) which is commercially produced as a by-product during the manufacture of silicon or silicon/metal alloys by an electro-metallurgical process. Its chemical compositions can vary slightly according to the characteristics of the process and of the main product, but it normally contains at least 86% by weight SiO₂ and 0.1 to 0.7% SiC. Grades of lower purity are not suitable for use in the present invention

50 50 because the quantity then required causes problems in de-watering the cement sheet material. Purer grades of relatively carbon-free volatilised silica are available, containing at least 94% SiO₂ and around 0.1% SiC. It has been found that these purer grades have a higher surface activity and hence can be used in smaller quantities than the normal grades, in the present invention. If the proportion of volatilised silica used in the sheet material of the present invention is less than 8% by weight, the volatilised silica must therefore be of a 55 55 grade containing more than 86% by weight SiO₂ and where the minimum proportion of 5% of volatilised silica is used, the latter material must contain at least 94% by weight SiO₂.

The preferred percentage of filamentised chopped glass fibre strands in the sheet material is from 3 to 4%. Although the percentage may be as low as 2%, problems can then arise in handling the green (*i.e.* uncured) sheet. With percentages between 4% and 7%, difficulties can be encountered in ensuring uniform dispersal

60 60 of the glass fibres in the cement matrix.

The balance of the composition may comprise up to 4% by weight of cellulose pulp, which is included as a processing aid to assist drainage. Up to 5% by weight of a plasticiser, for example ball clay, bentonite or talc, may also be incorporated to improve the plasticity of the material prior to curing. Small quantities of conventional dispersing and flocculating agents may also be used.

65 65 The filamentised strands are preferably made of an alkali-resistant glass composition containing at least 6 65

mol. % ZrO_2 . For example, the glass fibre strands may be of the type described and claimed in our U.K. Patent Specification No. 1,290,528 and sold by Fiberglass Limited under the Trade mark Cem-FIL, and their composition may be substantially, in mol. %

5	SiO_2	69%	5
	ZrO_2	9%	
	Na_2O	15.5%	
	CaO	6.5%	

10 The invention further provides a flat sheet material suitable for use as roofing slates, formed of a fibre-reinforced cement composition comprising, in percentages by weight of solids:-

15	Ordinary Portland cement	50 to 70%	15
	Pulverised fuel ash	20 to 40%	
	Volatilised silica (containing at least 86% by weight SiO_2)	8 to 12%	
	Filamentised chopped glass fibre strands	2 to 5%	

20 these components constituting at least 98% by weight of the solid constituents of the composition, the balance (if any) consisting of compatible constituents, the sheet material having a minimum average modulus of rupture of 20 N.mm^{-2} and a minimum density of 1.8 g.cm^{-3} , and a smooth surface for reception of a coating.

25 Tests on roofing slates made from such material have shown that they have a considerably better resistance to repeated freezing and thawing and general weathering than conventional asbestos cement slates.

25 The invention also resides in a method of making a sheet material of fibre-reinforced cement comprising the steps of mixing an aqueous slurry whose solid contents include:-

30	Ordinary Portland cement	50 to 71%	30
	Pulverised fuel ash	14 to 40%	
	Volatilised silica (containing at least 86% by weight SiO_2)	5 to 12%	
	Dispersible chopped glass fibre strands	2 to 7%	

35 in which these components constitute at least 90% by weight of the solid contents of the slurry and in which, when the slurry comprises less than 8% by weight of volatilised silica, the volatilised silica is of a grade containing more than 86% by weight SiO_2 , and when the slurry comprises only 5% by weight of volatilised silica, the volatilised silica is of a grade containing at least 94% by weight SiO_2 , the mixing being carried out so as to disperse the chopped glass fibre strands into single filaments, depositing a lamina from the slurry on 40 a foraminous surface, superimposing a plurality of said laminae on one another to build up a sheet of cementitious material, and curing the sheet.

40 In order to avoid mechanical damage to the glass fibres during processing, the slurry mixing may be carried out by first mixing the cement, pulverised fuel ash and silica with water in a high shear mixer and then adding the dispersible chopped glass fibre strands under low shear mixing conditions. Alternatively,

45 the slurry mixing may be carried out by first mixing the cement and pulverised fuel ash and optionally some of the silica with water in a higher shear mixer and then adding the silica or the remainder of the silica with the dispersible chopped glass fibre strands under low shear mixing conditions.

45 The deposition of the lamina and the building up of the sheet can be carried out on an asbestos-cement machine of the Bell or Hatschek type.

50 The sheet may be shaped to a desired cross-sectional profile before curing, e.g. so as to provide it with contiguous or spaced corrugations. The sheet may, for example, be shaped by application of a vacuum profiling head of known type, or by placing it on a former plate whose upper surface has the desired cross-sectional profile and allowing the sheet to collapse into contact with said surface. In the latter case, a second former plate may be placed over the sheet to complete the shaping.

55 The sheet may be cured at a temperature in the range from 60°C to 90°C , preferably from 70°C to 80°C , for 24 hours and then stored at ambient temperature for at least 7 days to complete the cure. Such a high temperature initial cure assists in ensuring the long term durability of the finished product, while the presence of the pulverised fuel ash and volatilised silica enables the filamentised glass fibre to survive the cure in sufficient quantity to provide adequate reinforcement.

60 The sheet may be pressed to de-water it before curing, e.g. by placing a stack of such sheets with interleaving plates in a press and subjecting the stack to pressure to expel water.

60 For making roofing slates, the shapes of the roofing slates are preferably stamped out from the sheet before it is pressed and cured and the slates are separated after curing.

65 Specific embodiments of the invention will now be described in more detail by way of example.

65 Sheet material in accordance with the invention, suitable for making roofing slates, can be made on

conventional asbestos cement machines of either the Bell type, as described in U.K. Published Patent Application No. 2,059,867A, or of the well-known Hatschek type. In both these machines, several laminae (typically eight) are superimposed to form a sheet of glass fibre reinforced cement with a thickness of 4 to 5 mm after pressing. In the case of the Bell machine, a glass fibre containing aqueous cement slurry is transferred through a doctor roll system on to a moving web or belt where it is de-watered to around 25% water content by suction. The lamina so formed is transferred from the belt on to a rotating drum. When sufficient laminae have been superimposed on one another on the drum to build up a sheet of the desired thickness, the sheet is cut off the drum. In the case of the Hatschek machine, the lamina is deposited on a rotating sieve and then transferred to a belt and thence to a drum. Again the sheet is cut off the drum once a sufficient number of laminae have been superimposed to build up the required thickness.

5 The subsequent processing is virtually the same in each case. A cutter is used to stamp out the shape of several flat rectangular roofing slates with their fixing holes on the sheet. The slates may be of the standard dimensions of 600 x 300 mm, or 500 x 250 mm, for example. The sheet is placed on a steel interleaving plate and transferred to a stack of similar sheets. When a sufficient number of stamped-out sheets have been 10 accumulated in the stack, it is passed to a press where the sheets are further de-watered by pressure to a final water content of about 20%. The interleaving plates are then removed and the sheets are cured at 80°C for 24 hours and finally stored at ambient temperature for seven days. The individual roofing slates can then be detached from one another and are ready for coating if desired.

15 The following specific Examples I and II relate to production of roofing slates in the above manner on a Bell machine.

20

Example I

An aqueous slurry was formulated having the following composition expressed as parts by weight of solids:-

25	Ordinary Portland cement	61%	25
	Pulverised fuel ash	25%	
	Volatilised silica (86% by weight SiO ₂)	9%	
30	Filamentised chopped strands of alkali-resistant glass fibre as sold under the Trade Mark "Cem-FIL" by Fibreglass Limited	3%	30
		2%	

Conventional dispersing agents, flocculating agents etc. may also be incorporated in small quantities (less than 0.1%) in known manner.

35 The glass fibre strands were substantially 3 mm in length, made up to filaments substantially 20 μ in diameter sized with a size composition designed to ensure that the strands disperse or filamentise in contact with the slurry. Examples of such sizes are disclosed in U.S. Patent Specification No. 3,948,673. The composition of the glass fibre was, in mol. %:-

40	SiO ₂	69%	40
	ZrO ₂	9%	
	Na ₂ O	15.5%	
	CaO	6.5%	

45 After curing as described above at 80°C for 24 hours and storage for seven days at ambient temperature, the slates were tested to ascertain their bending strengths in both the longitudinal and transverse directions relative to the direction of movement of the belt of the Bell machine; they were also tested for impact

strength. Further sample slates were subjected to accelerated ageing by total immersion in water at 70°C for sixteen days, simulating approximately 30 years natural weathering, and then re-tested. The results obtained were as follows:-

5

TABLE 1

5

			Longitu-	Trans-	Mean	
			dinal	verse		
10	Immediately	Limit of Proportionality (N.mm ⁻²)	22.9	12.6		10
		Modulus of Rupture (N.mm ⁻²)	25.8	15.1	20.5	
	cure	Impact Strength (Nmm.mm ⁻²)	-	-	3.2	15
20	accelerated	Limit or Proportionality (N.mm ⁻²)	28.7	16.0		20
		Modulus of Rupture (N.mm ⁻²)	29.7	17.3	23.5	
	ageing	Impact Strength (Nmm.mm ⁻²)	-	-	2.4	

Density of slates: 1.95 g.cm⁻³

25

It will be seen that the mean modulus of rupture was over 20 N.mm⁻² and increased after ageing.

25

Example II

Roofing slates were made up as described above from an aqueous cement slurry having the following composition expressed as percentages by weight of the solids content:-

30

35	Ordinary Portland cement	61%				
	Pulverised fuel ash	24.5%				
	Volatilised silica (86% by weight SiO ₂)	9%				
	Filamentised chopped glass fibre strands (as in Example 1)	3.5%				35
	Cellulose pulp	2%				
	Dispersing agents, flocculating agents etc.	<0.1%				

40 The slates produced were tested as in Example I with the following results:-

40

TABLE 2

			Longitu-	Trans-	Mean	
			dinal	verse		
50	Immediately	Limit of Proportionality (N.mm ⁻²)	24.6	15.9		45
		Modulus of Rupture (N.mm ⁻²)	25.8	16.5	21.2	50
	cure	Impact Strength (Nmm.mm ⁻²)	-	-	2.9	

Density of slates: 1.90 g.cm⁻³

Example III

Roofing slates were made up as in Examples I and II from an aqueous slurry having the following solids contents, by weight:-

5	Ordinary Portland cement	70%	5
	Pulverised fuel ash	14%	
	Volatilised silica (86% by weight SiO ₂)	11%	
	Filamentised chopped glass fibre strands (as in Example I)	3.5%	
10	Processing aids (cellulose pulp, dispersing agent, flocculating agent)	1.5%	10

Comparative Example IV

For comparison, a further set of slates were made up from a slurry made up as in Example III but with the 15 pulverised fuel ash replaced by limestone flour (CaCO₃).

15

Comparative Example V

For further comparison, roofing slates were made from a slurry whose solids contents were, by weight:-

20	Ordinary Portland cement	69%	20
	Pulverised fuel ash	6%	
	Volatilised silica (86% by weight SiO ₂)	20%	
	Filamentised chopped glass fibre strands (as in Example I)	3%	
25	Processing aids (cellulose pulp, dispersing agent, flocculating agent)	2%	25

Results of tests on the roofing slates of Example III and Comparative Examples IV and V were as follows:-

		Density	LOP	MOR	Impact	Specific MOR	
30	III						30
	Immediately after cure						
35		1.7	12.3	15.1	3.8	8.9	35
	After accelerated ageing	1.7	16.0	17.0	2.7	10.1	
40	IV						40
	Immediately after cure						
		1.7	12.6	15.4	4.0	9.1	
	After accelerated ageing	1.7	11.1	11.4	1.0	6.7	
45	V						45
	Immediately after cure						
		1.5	8.7	11.8	8.0	7.9	

It will be seen that the replacement of the pulverised fuel ash by limestone flour in Example IV gave much 50 reduced strength after ageing, while Example V with too much silica and insufficient pulverised fuel ash had poor strength even immediately after curing.

50

Example VI

This example relates to the production of a flat sheet of glass-fibre reinforced cement on a Hatschek machine, for use as a building panel, for which a minimum mean modulus of rupture (MOR) of 16 N.mm⁻² and a minimum density of 1.3 g.cm⁻³ may be specified.

5 The aqueous slurry had the following composition, in parts by weight:- 5

	Ordinary Portland Cement	60.5%	
	Pulverised fuel ash	24.5%	
	Volatile Silica (86% by weight SiO ₂)	8.0%	
10	Dispersible chopped glass fibre strands	3.5%	10
	Processing Aids (cellulose pulp, dispersing agent, flocculating agent)	3.5%	

The glass fibre strands were as described above in detail in Example I.

15 Sheets were formed in conventional manner on the Hatschek machine. Some of these sheets were profiled (i.e. corrugated) by use of a conventional profiling head and deposited on a correspondingly shaped former plate for curing. Other sheets were pressed to de-water them to a water content of 20% before curing. In each case the sheet was then cured at 80°C for 24 hours and stored for seven days thereafter at ambient temperature. Samples cut from the sheet were tested as described above to ascertain their bending 15

20 strengths, in both the longitudinal and transverse direction relative to the movement of the cylindrical sieve and belt of the Hatschek machine. They were also tested for impact strength. The results obtained were:- 20

TABLE 4

25 Profiled unpressed sheet: Dry density 1.4 g.cm⁻³ 25

		Longitudinal	Transverse	Mean	
30	LOP	13.8	12.6	13.2	
	MOR	22.4	16.7	19.6	30
	Impact	-	-	3.7	

Pressed flat sheet. Dry density 1.7 g.cm⁻³

		Longitudinal	Transverse	Mean	
35	LOP	18.7	16.9	17.8	
	MOR	31.8	19.8	25.8	35
	Impact	-	-	3.5	

40 Further trials have been made in the laboratory to investigate the range of possible compositions for the sheet material for making roofing slates. In such laboratory trials, with normal equipment, it is difficult to produce as thin a product as on the full scale machines and it is not possible to build up to the slate as a series of laminae or to obtain the same product density. The results obtained are useful in a comparative 40

45 sense though the absolute values obtained cannot be translated directly into values which would be obtained using similar formulations in full scale operation on a Bell or Hatschek machine. The laboratory trials were carried out by forming a slate, 30 cm square and 8 mm thick, and de-watering it by simultaneous application of pressure and suction. The slate was then cured at 60°C for 24 hours and the strengths measured as in the preceding Examples. The results are set out in Table 5, which also includes the 45

50 composition of each slate, the length of the glass filaments employed and a figure for the modulus of rupture corrected for the lower density of the slate as opposed to that to be expected for a slate produced from the same composition in full scale operation. In all these samples, volatile silica of at least 86% by weight SiO₂ content was used. 50

TABLE 5

Sample No.	OPC %	PFA %	Volatilised Silica %	Glass Fibre %	Filament length	Cellulose, dispersants, flocculants & C.	Density	LOP	MOR	Imp. act. strength	Specific MOR (Corrected for Density)
1	69	25	0	3.5	6 mm	2.5	1.68	7.3	13.1	2.5	7.8
2	69	14.5	11.5	3.5	6 mm	1.5	1.72	14.9	16.9	3.4	9.8
3	69	14.5	11.5	3.5	3 mm	1.5	1.72	18.3	20.3	4.0	11.7
4	62	28.5	5.0	3.0	3 mm	1.5	1.59	11.4	12.5	2.3	7.9
5	62	24	9.5	3.0	3 mm	1.5	1.66	15.4	16.8	3.3	10.1
6	57	29	9.5	3.0	3 mm	1.5	1.64	15.3	16.7	3.5	10.2
7	57	27	11	3.5	3 mm	1.5	1.67	15.2	16.6	4.7	9.9
8	52	32	11	3.5	3 mm	1.5	1.63	13.7	15.8	4.9	9.7
9	71	14	11	2.5	6 mm	1.5	1.68	14.9	16.1	3.4	9.6
10	81	0	10	3.0	3 mm	6.0	1.55	12.0	14.5	3.2	9.4

In the above Table, OPC = Ordinary Portland cement, PFA = Pulverised fuel ash, LOP = Limit of Proportionality and MOR = Modulus of rupture.

Of the ten samples tested, samples 1 and 10 are included only as comparative samples which are outside the scope of the invention because they contain no volatilised silica or pulverised fuel ash, respectively.

5 5 Sample 4 is also outside the scope of the invention because the content of volatilised silica is too low for use of a material of only 86% by weight SiO₂ content. The strengths obtained could be increased by increasing the temperature of cure and would certainly be increased in full scale operation due to the better distribution of the glass fibre which arises from the formation of individual laminae on the Bell and Hatschek machines.

10 Table 5 demonstrates that if the volatilised silica is not present (sample 1) the overall strength of the matrix is poor compared with those samples containing over 8% of the volatilised silica. Sample 10 shows that in the absence of pulverised fuel ash, the initial strength is low as compared with those samples containing equivalent amounts of volatilised silica; products made from such a composition, when subjected to artificial ageing, show a further falling off in strength. The strength of sample 4 would be substantially increased if volatilised silica of 94% SiO₂ content were used in accordance with the invention.

15 15 To demonstrate the importance of using volatilised silica of 94% SiO₂ content rather than 86% SiO₂ content when the proportion of volatilised silica in the material is relatively low, a series of samples were made in the laboratory, differing only in the type and proportion of volatilised silica, and tested for LOP and MOR, with the following results. Two grades of volatilised silica containing 86% SiO₂ and one containing 94% SiO₂, identified in the Tables as Grades 1, 2 and 3, were used.

20 20

TABLE 6A

			LOP	MOR	
25	8½%	Volatile Silica (86% SiO ₂)	(Grade 1)	12.6	15.3
	6½%	Volatile Silica (86% SiO ₂)	(Grade 1)	11.1	13.4
	5½%	Volatile Silica (86% SiO ₂)	(Grade 1)	10.4	12.4

TABLE 6B

			LOP	MOR	
30	8½%	Volatile Silica (86% SiO ₂)	(Grade 1)	10.6	13.2
	8½%	Volatile Silica (86% SiO ₂)	(Grade 2)	10.8	13.6
	6½%	Volatile Silica (86% SiO ₂)	(Grade 2)	10.3	12.5
	5½%	Volatile Silica (86% SiO ₂)	(Grade 2)	8.6	11.4

			LOP	MOR	
35	8½%	Volatile Silica (86% SiO ₂)	(Grade 1)	10.6	12.2
	8½%	Volatile Silica (94% SiO ₂)	(Grade 3)	9.6	12.5
	6½%	Volatile Silica (94% SiO ₂)	(Grade 3)	9.4	12.0
	5½%	Volatile Silica (94% SiO ₂)	(Grade 3)	9.5	12.0

TABLE 6C

			LOP	MOR	
40	8½%	Volatile Silica (86% SiO ₂)	(Grade 1)	10.6	12.2
	8½%	Volatile Silica (94% SiO ₂)	(Grade 3)	9.6	12.5
	6½%	Volatile Silica (94% SiO ₂)	(Grade 3)	9.4	12.0
	5½%	Volatile Silica (94% SiO ₂)	(Grade 3)	9.5	12.0

45 45 It will be seen that reduction of the silica content from 8½% to 5½% was accompanied by a substantial loss of strength where 86% SiO₂ content volatilised silica was used, but that with the 94% SiO₂ content volatilised silica no appreciable loss of strength resulted.

50 50 CLAIMS

50 1. A sheet material formed of a fibre-reinforced cement composition comprising, in percentages by weight of solids:-

55	Ordinary Portland cement	50 to 71%	
	Pulverised fuel ash	14 to 40%	
	Volatile silica (containing at least 86% by weight SiO ₂)	5 to 12%	
	Filamentised chopped glass fibre strands	2 to 7%	

60 60 60 in which these components constitute at least 90% by weight of the solid constituents of the composition and in which, when the cement composition comprises less than 8% by weight of volatilised silica, the volatilised silica is of a grade containing more than 86% by weight of SiO₂, and when the cement composition comprises only 5% by weight volatilised silica, the volatilised silica is of a grade containing at least 94% by weight SiO₂, the sheet material having a minimum average modulus of rupture of 16 N.mm⁻² and a minimum density of 1.3 g.cm⁻³.

65

2. A sheet material according to Claim 1 wherein the weight percentage of filamentised chopped glass fibre strands is from 3 to 4%.

3. A sheet material according to Claim 1 or 2, wherein the balance of the composition comprises up to 4% by weight of cellulose pulp.

5 4. A sheet material according to any one of the preceding claims wherein the filamentised chopped glass fibre strands are made of an alkali-resistant glass composition containing at least 6 mol. % ZrO_2 .

5 5. A sheet material according to Claim 4, wherein the composition of the glass fibre strands is substantially, in mol. %:-

10	SiO_2	69%
	ZrO_2	9%
	Na_2O	15.5%
	CaO	6.5%

15 6. A flat sheet material suitable for use as roofing slates, formed of a fibre-reinforced cement composition comprising, in percentages by weight of solids:-

15	Ordinary Portland cement	50 to 70%
	Pulverised fuel ash	20 to 40%
20	Volatile silica (containing at least 86% by weight SiO_2)	8 to 12%
	Filamentised chopped glass fibre strands	2 to 5%

25 these components constituting at least 98% by weight of the solid constituents of the composition, the balance (if any) consisting of compatible constituents, the sheet material having a minimum average modulus of rupture of 20 N.mm^{-2} and a minimum density of 1.8 g.cm^{-3} , and a smooth surface for reception of a coating.

25 7. A method of making a sheet material of fibre-reinforced cement comprising the steps of mixing an aqueous slurry whose solid contents include:-

30	Ordinary Portland cement	50 to 71%
	Pulverised fuel ash	14 to 40%
	Volatile silica (containing at least 86% by weight SiO_2)	5 to 12%
35	Dispersible chopped glass fibre strands	2 to 7%

40 in which these components constitute at least 90% by weight of the solid contents of the slurry and in which, when the slurry comprises less than 8% by weight of volatile silica, the volatile silica is of a grade containing more than 86% by weight SiO_2 , and when the slurry comprises only 5% by weight of volatile silica, the volatile silica is of a grade containing at least 94% by weight SiO_2 , the mixing being carried out so as to disperse the chopped glass fibre strands into single filaments, depositing a lamina from the slurry on to a foraminous surface, superimposing a plurality of said laminae on one another to build up a sheet of cementitious material, and curing the sheet.

45 8. A method according to Claim 7, wherein the slurry mixing is carried out by first mixing the cement, pulverised fuel ash and silica with water in a high shear mixer and then adding the dispersible chopped glass fibre strands under low shear mixing conditions.

45 9. A method according to Claim 7, wherein the slurry mixing is carried out by first mixing the cement and pulverised fuel ash and optionally some of the silica with water in a high shear mixer and then adding the silica or the remainder of the silica with the dispersible chopped glass fibre strands under low shear mixing conditions.

50 10. A method according to any of Claims 7 to 9, wherein the deposition of the lamina and the building up to the sheet are carried out on an asbestos-cement machine of the Bell or Hatschek type.

50 11. A method according to any one of Claims 7 to 10, wherein the sheet is shaped to a desired cross-sectional profile before curing.

55 12. A method according to Claim 11, wherein the sheet is shaped by application of a vacuum profiling head of known type.

55 13. A method according to Claim 11, wherein the sheet is shaped by placing it on a former plate whose upper surface has the desired cross-sectional profile and allowing the sheet to collapse into contact with said surface.

60 14. A method according to Claim 13 wherein a second former plate with the said profile is placed over said sheet.

60 15. A method according to any one of Claims 7 to 14, wherein the sheet is cured at a temperature in the range from $60^\circ C$ to $90^\circ C$ for 24 hours and then stored at ambient temperature for 7 days to complete the cure.

65 16. A method according to Claim 15, wherein the sheet is cured at a temperature in the range from $70^\circ C$ to $80^\circ C$.

17. A method according to any one of Claims 7 to 16, wherein the sheet is pressed to de-water it before curing.
18. A method according to Claim 17, for making roofing slates, wherein the shapes of the roofing slates are stamped out from the sheet before it is pressed and cured and the slates are separated after curing.
- 5 19. A roofing slate substantially as hereinbefore described in any one of Examples I, II and III.
20. A method of making roofing slates substantially as hereinbefore described in any one of Examples I, II and III.
21. A sheet material substantially as hereinbefore described in Example VI.
22. A method of making a sheet material substantially as described in Example VI.

Printed in the UK for HMSO, D8818935, 4-85, 7102.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.